Improvement of microbial fuel cell cathodes using cost-effective polyvinylidene fluoride

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HIGHLIGHTS

- Polyvinylidene fluoride (PVDF) was tested as a new and effective diffusion layer for cathode.
- PVDF cathode produced higher power density and CE than PTFE cathode.
- Cathode with 4 PVDF DLs had an improved three-phase interface and produced the largest MPD.

ARTICLE INFO

ABSTRACT

In this study polyvinylidene fluoride (PVDF) is investigated as an alternative to polytetrafluoroethylene (PTFE) for air-cathode diffusion layers (DLs) in microbial fuel cells (MFCs) for the improvement of MFC power generation. It is found that the cathode fabricated with PVDF achieves a higher maximum power density (MPD) than a PTFE cathode. Successive PVDF or PVDF/carbon black DLs are applied on the base layers in order to optimize cathode performance. The results show significant improvements in such performances as the coulombic efficiency (CE), MPD, and water loss. In electrochemical tests, the cathode coated with four PVDF DLs has the largest current response at a given applied potential, yielding the highest MPD of 0.123 mW cm^{-2} (normalized to the projected cathode surface area) and largest CE (10.7%) in the MFC test. Carbon black is added to the DLs in order to test its effect on the MFC power generation. Cathodes made from pure PVDF DLs perform better than those containing PVDF/carbon black DLs in electrochemical and MFC tests. In addition, a smaller MFC (28 mL) produces a much higher MPD than a larger MFC (700 mL), resulting in an increase in the CE.

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1. Introduction

As a promising environmentally friendly technology, microbial fuel cells (MFCs) have attracted increasing attention in areas of wastewater treatment and electricity generation [1–4]. Various oxidants, such as ferricyanide [5,6] and permanganate [7], have been applied as electron acceptors in MFCs. However, oxygen is considered to be the most suitable electron acceptor in wastewater treatment because of its free availability, sustainability, and non-pollutive properties. Therefore, due to their simple structure and direct use of oxygen in ambient air, devices such as air-cathode MFCs have the greatest potential in practical applications involving wastewater treatment [8].

The air-cathode can affect the power production of an MFC due to the poor kinetics of oxygen reduction at the cathode catalytic sites under typical MFC operating conditions (ambient temperature and neutral pH) [9]. Moreover, oxygen transport through the cathode is restricted because of the porous structure of the cathode and low solubility and diffusivity of oxygen in water. The cathodic performance and cathode surface area have been proven to be the two most important factors affecting maximum power densities (MPDs) in many MFCs [10–14]. On the other hand, the expense of the cathode accounts for a large part of the complete MFC cost, which hinders the practical application of MFC technologies. Therefore, exploiting cost-effective cathodic materials and designing efficient cathodes for improving MFC performance are two main challenges still to be met.

Currently, most air-cathodes are made on a base of carbon cloth, using polytetrafluoroethylene (PTFE) as diffusion layers (DLs) on the air-facing side of the cathodes to control oxygen intrusion and

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eliminate water loss [1,9]. By this approach, the performances of MFCs, in terms of increasing coulombic efficiencies (CEs) and MPDs as well as reducing water losses through the cathodes, can be greatly improved [9,15,16]. However, a high temperature of 370 °C must be supplied to meet the requirements of cathode fabrication with PTFE, which leads to a large waste of energy [9].

An alternative material with similar chemical and physical properties to PTFE is expected to further improve the power production and reduce the expense of cathodes. Polyvinylidene fluoride (PVDF) is a highly non-reactive and pure thermoplastic fluoropolymer produced by the polymerization of vinylidene difluoride. It is universally used in the fields of chemistry, semiconductors, medicine, defense technology, and lithium ion batteries [17,18]. The electron cloud in the monomer molecules of PVDF distributes symmetrically, making PVDF highly hydrophobic and waterproof. More importantly, the PVDF has a lower melting point, which should make it possible to reduce the temperature during the cathode fabrication process. To test this hypothesis, we examined the use of this new polymer in cathodes and investigated their performances in terms of water loss and power generation. We varied the amount of PVDF applied on the carbon-supporting material to optimize cathode performance. To our knowledge, this is the first report using PVDF in DLs of air-cathodes for MFCs.

2. Materials and methods

2.1. Cathodes fabrication

The newly developed cathodes applied carbon cloth (CC, HCP331N, Hesen, China) as the supporting material. The fabrication procedure was modified from Cheng's method [9]. The PVDF/carbon base layer was prepared by applying a mixture of carbon black powder (Alfa Aesar, USA) and PVDF solution (10 μL 18 wt % PVDF per mg of carbon black power) onto the air-facing side of carbon cloth, air-drying at room temperature for 2 h, followed by heating at 250 °C for 20 min. Carbon loading in the base layer was 1.56 mg cm^{-2}. Multiple PVDF layers containing PVDF solution (18 wt %) were coated on top of base layer (0.9 mg cm^{-2} of PVDF for every coating), followed by air-drying at room temperature and heating at 250 °C for 5 min. The cathode DLs were fabricated by applying PVDF layers for 2, 4, 6, 8 times, producing the cathodes of L2, L4, L6 and L8. PVDF/carbon black layers (one to four layers) were applied on top of the previous PVDF/carbon base layer on carbon cloth at the same mass loading as the base layer, producing another four cathodes of C-L1, C-L2, C-L3 and C-L4. After each layer has been applied, the cathodes were air-dried and heated at 250 °C for 5 min. Carbon cloth cathodes with four PTFE DLs were also prepared following previously described method [9]. When the fabrication of DLs finished, Pt catalyst (0.2 mg cm^{-2}, 40% Pt Hesen, China) was then applied to the water-facing side of all cathodes as previously described [19].

2.2. MFC construction and operation

Cylindrical Plexiglas tube single-chamber MFCs (height: 12 cm, diameter: 9 cm, working volume: 700 mL) with air-cathodes were used in this study. Graphite felt (5 cm × 5 cm × 0.5 cm, Beijing Sanye Carbon Co., Ltd) was used as the anode electrode. After being soaked in acetone for 4 h and rinsed with deionized water, the graphite felt was heated at 400 °C for 1 h. These anodes were fixed by titanium wire in the center of the anode chambers, orienting parallel to cathodes. The cathodes with 4 cm in diameter were clamped by flanges. Titanium sheet was used to connect the circuit. The L2 cathode was also examined in a smaller single chamber

cubic-shaped MFC (anode chamber with 4 cm in length and 3 cm in diameter) to compare the power production performance with the larger MFC (700 mL).

Each MFC reactor was inoculated using mixed cultures enriched from cracked cereals, which were dominated by *Clostridium pasteurianum* [6]. The MFCs were initially inoculated with a mixture (1:4 in volume) of inoculum and nutrient medium before stable voltages were obtained. When biofilm formed on the anode surface, the solution was switched to only nutrient medium. Nutrient medium (per liter) contained: sucrose, 1000 mg; NH_4HCO_3, 500 mg; Na_2CO_3, 2000 mg; $NaH_2PO_4 \cdot 2H_2O$, 3978 mg; $Na_2HPO_4 \cdot 12H_2O$, 8771 mg; K_2HPO_4, 125 mg; $MgCl_2 \cdot 6H_2O$, 100 mg; trace minerals (12.5 mL L^{-1}) and vitamins (5 mL L^{-1}) [20]. The initial COD and pH of the anolyte were 1122 mg L^{-1} and 7.70, respectively. MFCs were operated in fed-batch mode at 35 °C.

2.3. Analytics and calculation

Voltage (*E*) across the external resistor (1000 Ω, except as noted) in the MFC circuit was continuously measured at 5 min intervals using a data acquisition system (CT-3008-5V50 mA-S4, Xinwei, China). Current (*I*) was calculated by $I = E/R_e$, where R_e represents the external resistance; power (*P*) was calculated as $P = IE$ as previously described [21]. External resistances were changed from 1000 to 50 Ω in decreasing order, with every 30 min for each external resistance, in order that the polarization and power density curves of the larger MFCs can be obtained. For the smaller MFC, each resistor was used for a full fed-batch cycle. The CE was calculated as CE (%) = $C_p/C_t \times 100\%$, where C_p is produced coulombs that calculated by integrating the current over time, and C_t is the theoretical amount of coulombs based on COD removal [21]. Overall energy recovery was calculated as NER = E_p/V_a (or COD), where E_p (kWh), is the produced total energy calculated by integrating the power over time, V_a is the anode liquid volume and COD is the removed COD within a batch operation.

Electrochemical property and impedance behavior of the cathodes were studied by linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) using an electrochemical workstation (CHI 604E, ChenHua Instruments Co., Ltd., Shanghai, China). LSV test was conducted in the absence of bacteria and substrate. A three-electrode system was used for measurements, consisting of a working electrode (cathode with 12.56 cm^2 projected surface area), a counter electrode (Pt wire) and an Ag/AgCl reference electrode (218, Shanghai REX Instrument Factory). Potential was scanned from 0.3 to −0.3 V (vs. Ag/AgCl electrode) with scan rate of −1 mV s^{-1}.

EIS tests were performed at the end of a batch operation and conducted at polarized conditions of 0 V, −0.1 V, and −0.2 V (vs. Ag/AgCl), which were similar to the operating potentials of the cathodes in MFCs, over a frequency range of 100 kHz to 10 mHz with a sinusoidal perturbation of 10 mV amplitude [10]. EIS is a useful electrochemical technology that can be employed to measure the internal resistance (R_{int}) of the cathode [22,23]. Total cathode resistance, including charge transfer resistance (R_{ct}), diffusion resistance (R_d) and solution resistance (R_s), were determined by fitting and simulating the measured impedance data to an equivalent electrical circuit using Zview 2.0 software.

Oxygen permeability of a cathode was calculated in terms of oxygen transfer coefficient (*k*) as previous report [9]. Oxygen concentrations were continuously measured at 30 min intervals for 5 h using a dissolved oxygen probe (OHAUS STARTER 300D, USA), which was fixed in the center of the anode chamber filled with oxygen-free deionized water.

3. Results and discussion

3.1. Performance of cathodes in MFC tests

MFC tests were conducted to compare the performance of the PVDF cathode with that of the PTFE cathode. After a short lag period, the MFC with the PVDF cathode produced a maximum voltage of 569 mV, which was 44 mV higher than that produced by the PTFE cathode. During the operation, a stable voltage generation (520–550 mV) was produced by the MFC with the PVDF cathode, but the voltage output of the MFC using the PTFE cathode varied over a large range from 335 mV to 520 mV. Polarization tests showed that the MPD of 0.035 mW cm^{-2} was obtained from the MFC with the PVDF cathode, which was 8.5% higher than that with the PTFE cathode (Fig. 1A). The MFC with the PVDF cathode showed slightly higher chemical oxygen demand (COD) removal and CE than that with the PTFE cathode, likely due to the higher oxygen transfer coefficient of the PVDF cathode (Table 1).

All MFCs with carbon cloth cathodes using Pt catalyst immediately produced voltages after inoculation and generated stable voltages at a fixed resistance of 1000 Ω. The maximum voltages of all the MFCs were similar (Fig. 2A and B), but there were significant differences in the duration of each batch among these reactors. The MFCs using the cathodes with two and four DLs (L2 and L4 cathodes) remained in a stable electricity-generation state over 450 h, which was much longer than the other two MFCs (L6 and L8). The voltages of the MFCs using cathodes with PVDF/carbon black DLs remained stable for a shorter time period (<250 h).
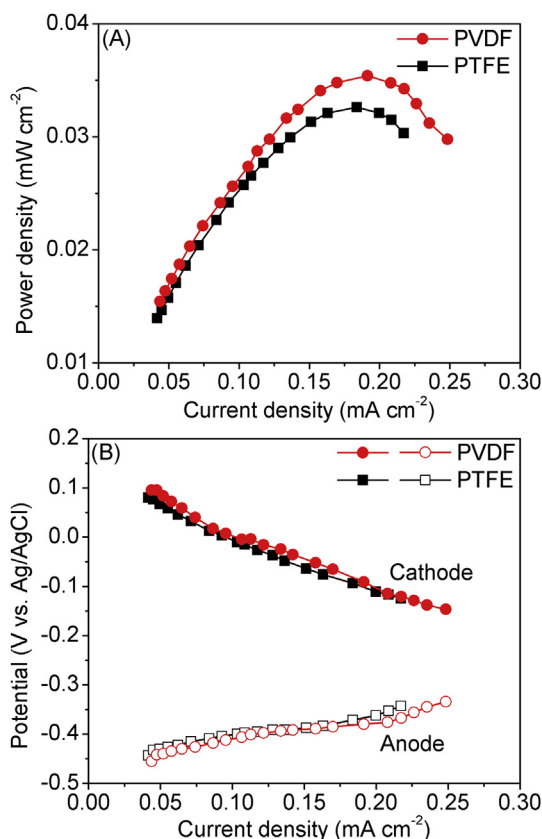
Table 1
COD removal and coulombic efficiencies of MFCs with the cathodes and oxygen transfer coefficients (k) of the cathodes.

Cathode type	COD removal (%)	CE (%)	Oxygen transfer coefficient (k)
PVDF	96	4.9	$1.13 \pm 0.09 \times 10^{-3}$
PTFE	91	4.2	$1.08 \pm 0.05 \times 10^{-3}$

Large differences in power production among the cathodes with different DLs were observed based on polarization data. The largest MPD of 0.123 mW cm^{-2} was obtained from the L4 cathode at a current density of 0.44 mA cm^{-2}, which was 108%, 35%, and 75% greater than those obtained from the L2, L6, and L8 cathodes, respectively (Fig. 3A). As shown in Fig. 3C, the MPDs of MFCs employing cathodes with PVDF/carbon black DLs varied over a range of 0.074–0.097 mW cm^{-2} at current densities of 0.26–0.33 mA cm^{-2}. These MPDs were in reverse order with the number of layers applied on the base layer. With the same cathode, the MPD produced with the L4 cathode in the experiment to optimize the number of DLs was much higher than that obtained in the comparison experiment of PVDF and PTFE due to the acclimation of the anode biofilm during the long operation period of the optimization experiment. This behavior was demonstrated by decreased overpolarization of anodes in the optimization experiment (Fig. 3B). Moreover, a smaller MFC (SMFC, 28 mL) with the L2 cathode produced an MPD as high as 0.084 mW cm^{-2}, which was 42% higher than that produced by the larger MFC (700 mL).

Polarization tests showed that the anode performances were almost identical among the MFC reactors with different cathodes (Fig. 3B and D), providing evidence that the cathode performances
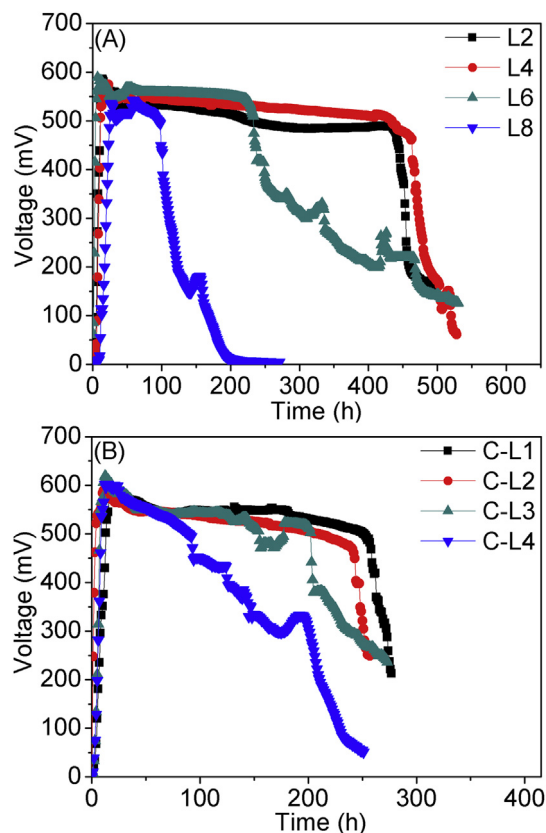

Fig. 1. Power densities (A) and electrode potentials (B) of the cathodes with Pt catalyst and four layers of PVDF DLs or four PTFE DLs as a function of current density (normalized to cathode surface area) obtained by varying the external circuit resistance (1000–50 Ω).

Fig. 2. Voltage generation of MFCs using the cathodes with PVDF DLs (A) and PVDF/carbon black DLs (B) vs. time, with 50 mM PBS buffer and 1.0 g L^{-1} sucrose.
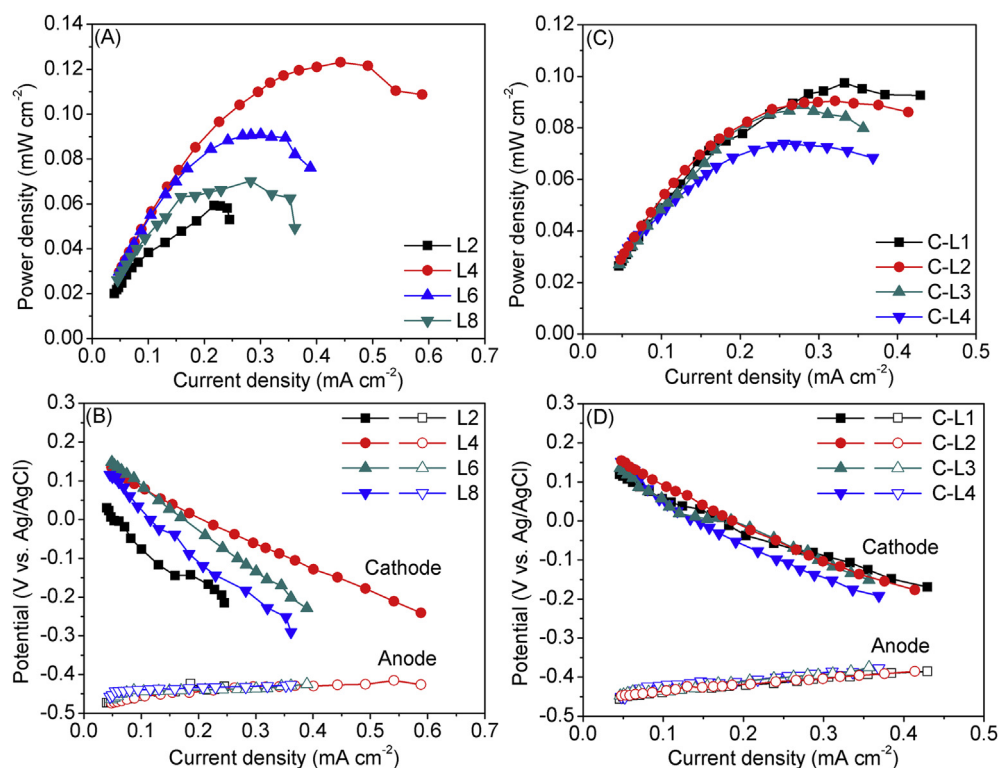
Fig. 3. Power densities (left column) and electrode potentials (right column) of the cathodes with PVDF DLs (A), (B) and PVDF/carbon black DLs (C), (D) as a function of current density (normalized to cathode surface area) obtained by varying the external circuit resistance (1000–50 Ω).

were the reason for the differences in power generation among these reactors. The increase in MPD upon application of additional PVDF DLs on the base layer probably resulted from an improved three-phase interface for oxygen reduction by the Pt catalyst [9]. The largest MPD of 0.123 mW cm^{-2} was achieved with the L4 cathode, which was attributed to the improved oxidation reduction reaction at the optimal three-phase interface. However, further addition of PVDF DLs destroyed the optimal structure of the three-phase interface, which resulted in worse electrochemical performance and thus had an adverse effect on power generation. The largest MPD of 0.097 mW cm^{-2} using cathodes with PVDF/carbon black DLs was achieved with the C-L1 cathode, but this MPD was less than that obtained with the L4 cathode. The reduced performance likely resulted from the increased oxygen flow to the anode chamber through the cathode where bacteria preferentially used oxygen directly as an electron acceptor instead of using the anode as the electron acceptor. Quan et al. [24] reported that the infusion of oxygen from the air-cathode decreased the voltage output and shortened cycle periods, resulting in a reduction in the CE. The MPDs using the cathodes with PVDF/carbon black DLs varied over a smaller range of 0.074–0.097 mW cm^{-2}, whereas those obtained using cathodes with only PVDF DLs showed much wider variation. Thus, the number of PVDF/carbon black DLs had less effect on power generation than the number of only PVDF DLs. Equipped with the L2 cathode, the larger MFC achieved a lower MPD than the smaller MFC, indicating that scaling-up the MFC reactor would reduce the power density. It was possible that many important factors affecting power generation were changed, such as increased electrode spacing, decreased electrode specific surface area (surface area per volume), and a greater internal resistance [12]. The highest MPD (0.123 mW cm^{-2}) obtained in this study was higher than the best performance achieved using the 520-mL reactor with complicated construction and high anode surface area

(0.052 mW cm^{-2}) [12], and also higher than the best result of a 1.5-L reactor with two air-cathode groups on opposing sides (0.016 mW cm^{-2}) [25]. These results imply the excellent performance of PVDF in MFCs, favoring their use in practical applications as the DLs in MFC cathodes.

3.2. Oxygen permeability of the cathodes

PVDF is relatively permeable to oxygen. Oxygen diffusion into the anode chamber was reduced with the successive application of PVDF (or PVDF/carbon black) DLs due to the increased thickness of the DLs. The C-L1 cathode had the highest oxygen mass transfer coefficient (k) of $2.60 \pm 0.06 \times 10^{-3}$ cm s^{-1} (Fig. 4). When four
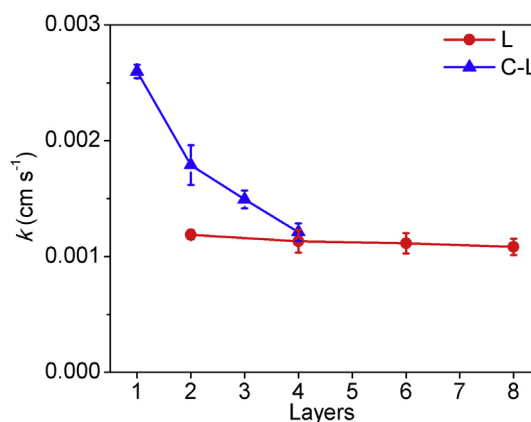

Fig. 4. Oxygen transfer coefficients (k) of the cathodes with PVDF DLs (L) and PVDF/carbon black DLs (C–L). (Error bars ± SD based on two measurements.)

PVDF/carbon black DLs were applied, the k value of the C-L4 cathode decreased to $1.21 \pm 0.08 \times 10^{-3}$ cm s^{-1}. The k values of the four cathodes applied with only PVDF DLs ranged from $1.08 \pm 0.07 \times 10^{-3}$ cm s^{-1} to $1.19 \pm 0.04 \times 10^{-3}$ cm s^{-1}. Cathodes covered by PVDF/carbon black DLs exhibited higher permeability than those with DLs of pure PVDF (without carbon black), which was probably due to the synergistic effects of the coarse surface, the large porosity of carbon cloth, and the high oxygen permeability of the microporous hydrophobic layer formed during the application of the PVDF/carbon black DLs on the base layer [26]. The four k values of these cathodes were higher than those reported previously when the cathodes used stainless steel mesh as the supporting material and a current collector with poly(dimethylsiloxane) (PDMS) DLs [26], indicating the higher oxygen permeability of PVDF.

3.3. Performance of cathodes in electrochemical tests

The electrochemical performances of the cathodes were evaluated in the absence of bacteria using LSV tests before the operation of MFC tests. The current densities of the cathodes increased in magnitude as the overpotentials of the cathodes increased. As illustrated in Fig. 5A, for the cathodes made of only PVDF (without carbon black), successive application of PVDF DLs increased the current densities for up to four PVDF layers (L4), but further addition of DLs (L6 and L8) decreased the current responses. Voltammograms were also obtained for the cathodes containing PVDF/carbon black DLs. These cathodes with one to four additional DLs showed poorer electrochemical performance than those with only PVDF DLs, and all had similar current densities at a given applied potential (Fig. 5B). The current densities of the cathodes with two to four PVDF/carbon black DLs were slightly less than that of the C-L1

Fig. 5. LSV of the cathodes with PVDF DLs (A) and PVDF/carbon black DLs (B).

cathode. The small variation in electrochemical performance among these cathodes was similar to that obtained in a previous investigation in which PDMS and carbon black were used as DLs [26]. Zhang et al. [26] pointed out that the cathodes applied with PDMS/carbon black had higher current densities than those with only PDMS. However, in this study, we found that the cathodes with PVDF/carbon black DLs showed lower electrochemical activities than those covered with pure PVDF DLs, which is inconsistent with the finding of the previous study. These results indicate that although both PVDF and PDMS are hydrophobic materials, there are significant differences in their molecular structures, and thus, the electrochemical properties of PVDF are different from those of PDMS. The higher oxygen permeability of cathodes with PVDF/carbon black DLs indicated that the additional carbon black in DLs might form a microporous hydrophobic layer. This special porous structure had adverse effects on the electrochemical activities of the cathode. Thus, the increased porosity in DLs failed to improve the electrochemical performance of the cathodes with PVDF/carbon black DLs.

3.4. Resistances of electrodes

Electrochemical impedance spectroscopy (EIS) was conducted at polarized conditions of 0 V, −0.1 V and −0.2 V (vs. Ag/AgCl). As the oxygen reduction overpotential increased, the total cathode impedance decreased, which was illustrated by the decrease in the size of the semi-circle shown in Nyquist plots. This occurred because of the increasing kinetic driving force of larger overpotentials. The impedance of the L4 cathode was smaller than the other three cathodes with PVDF DLs at all polarized conditions, as shown by the smallest semi-circle produced in Nyquist plots (Fig. 6A, C and E). The four cathodes with PVDF/carbon black DLs had a much narrower variation in impedance than the cathodes with pure PVDF DLs, and the C-L1 cathode showed slightly less impedance than the cathodes with additional PVDF/carbon black DLs (Fig. 6B, D and F).

The individual components of the cathode internal resistance were calculated by fitting the EIS spectra to an equivalent circuit as previously described [27]. The equivalent circuit model (Fig. 7) used here assumed that the cathode performance was affected by both reaction kinetics and diffusion. Solution resistances (R_s) were similar for the cathodes at different polarized conditions, which could be explained by the use of the same cell configuration and solution (Fig. 8). This type of resistance could be reduced by increasing the concentration of anolyte solution and improving the structure of the MFC reactor. Generally, charge transfer resistance (R_{ct}) is a minor contributor to the total cathode internal resistance. However, the cathodes with PVDF/carbon black DLs showed larger R_{ct}s than those with PVDF DLs, which could be attributed to the fact that additional PVDF/carbon black DLs formed a hydrophobic porous layer that impeded electron transfer and thus resulted in poor electrical conductivity. The L4 cathode possessed the smallest R_{ct} at all three polarized conditions, ensuring its best performance in the MFC test. Diffusion resistances (R_d) also decreased from a high potential of 0 V to a low potential of −0.2 V for all of the cathodes. The R_d of the L2 cathode was much higher than those of the other three cathodes at all three potentials, leading to its poorest performance in power generation. The R_d of the cathodes with PVDF DLs varied largely at every polarized condition, indicating the great influence of the PVDF DLs on the diffusion resistance of cathodes. However, there were small variations among the cathodes with PVDF/carbon black DLs at each potential. In a previous study, the difference in R_d between two types of cathodes was attributed to different anti-flooding properties between the two catalyst binders [10]. Nevertheless, there were also variances
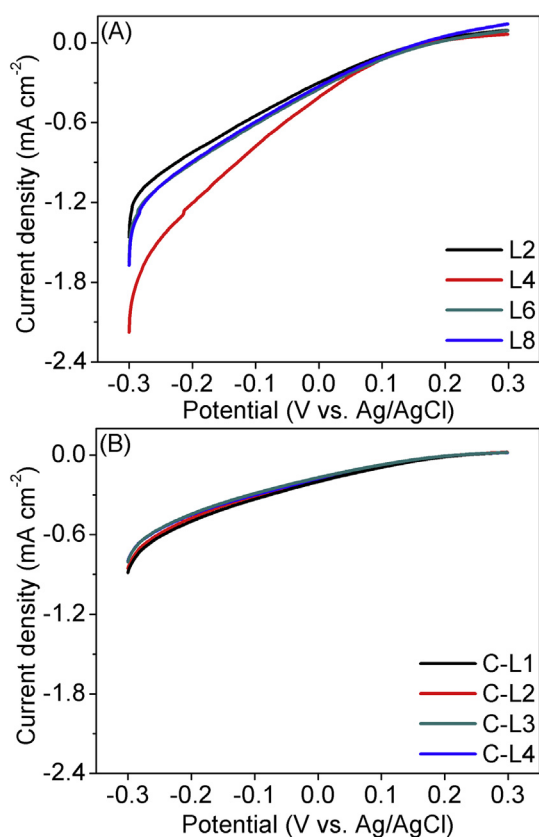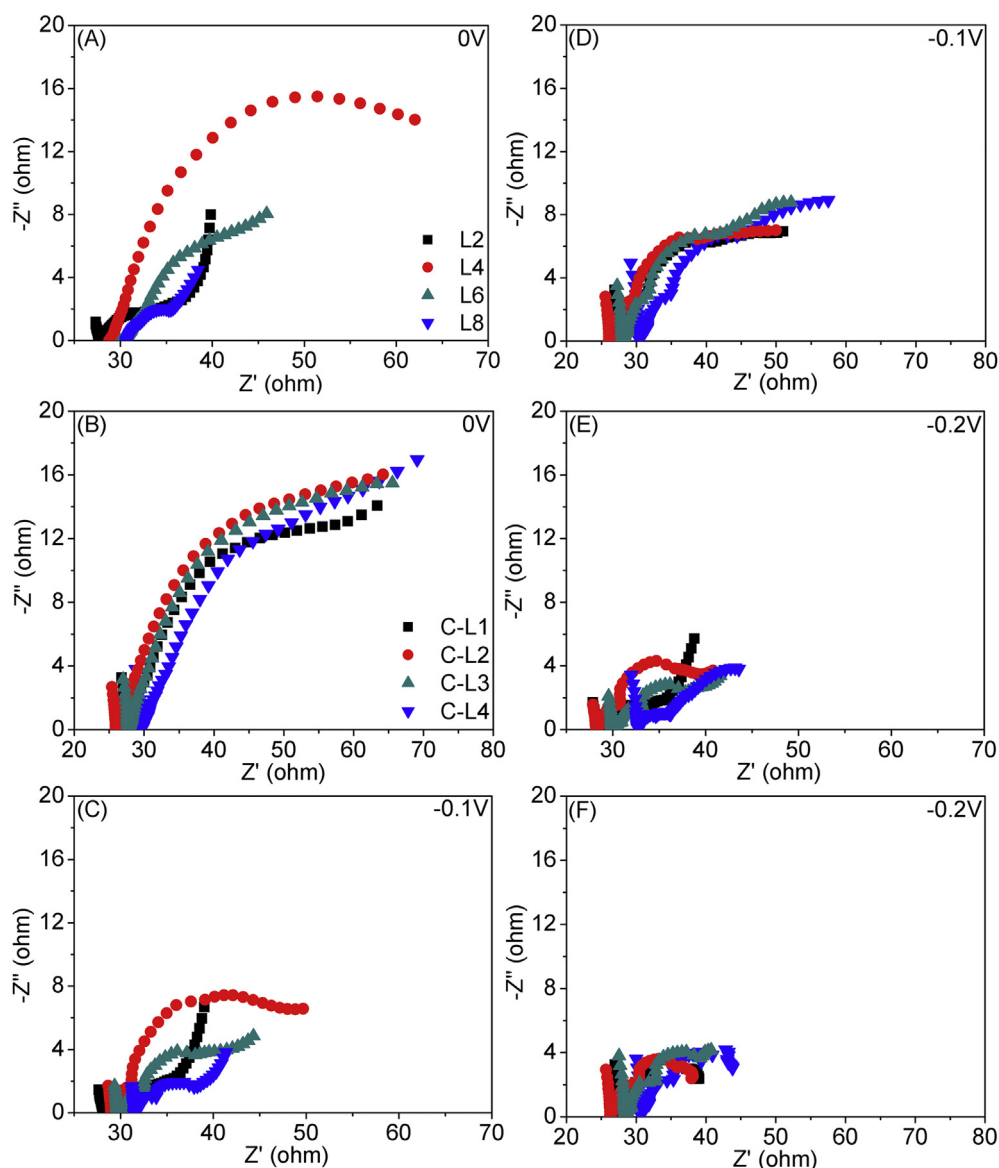
Fig. 6. Nyquist plots of EIS spectra by the cathodes with PVDF DLs (left column) and PVDF/carbon black DLs (right column) at different cathode potentials of 0 V, −0.1 V and −0.2 V (vs. Ag/AgCl).

among the cathodes with the same catalyst binder but different types of DLs. Therefore, we ascribed the variances to the special structure of DLs that formed during the cathode fabrication and then facilitated the proton and oxygen diffusion to the catalyst.

3.5. COD removal, CE, and normalized energy recovery

There were little variations in COD removal over a cycle of operation, ranging from 87% to 93%, and the number of DLs had no
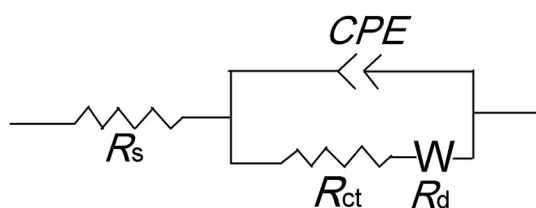

Fig. 7. Equivalent circuit for modeling the EIS of the cathodes.

effect on COD removal. Larger MFCs using the cathodes with PVDF DLs produced higher CEs, except for the MFC with the L8 cathode, whereas the cathodes with PVDF/carbon black DLs generated lower CEs due to the higher oxygen permeability of these cathodes that allowed abundant oxygen invasion into the anode chambers. Oxygen in the anode chamber facilitated the growth of heterotrophic bacterial and consumption of the substrate. The CEs generated with the cathodes in larger MFCs ranged from 2.5% to 10.7% (Table 2), and these values were similar to those of 9%−12% obtained in glucose-fed MFCs [16]. However, the volumes of those MFC reactors (28 mL) were substantially smaller than the volumes used here. When a smaller MFC was employed to produce electricity, the CEs increased, ranging from 11.7% to 37.7% at current densities of $0.07-0.50$ mA cm^{-2}. The relatively low CEs obtained here could be due to the use of sucrose as the substrate and the long operation time per batch (250−500 h). Sucrose, as a fermentable sugar, facilitates processes such as fermentation and methanogenesis, which are likely competitors to electricity generation in the anode chamber. In addition, the long operation time allowed more oxygen
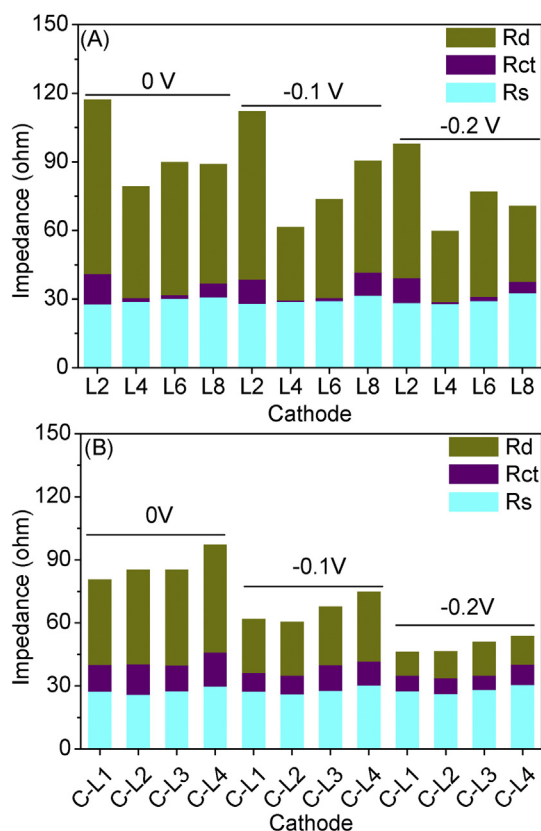
Fig. 8. Individual component analysis of cathode internal resistance at different EIS operation conditions for the cathodes with PVDF DLs (A) and PVDF/carbon black DLs (B).

Table 2
COD removal and coulombic efficiencies of MFCs with the cathodes.

Cathode type	L2	L4	L6	L8	C-L1	C-L2	C-L3	C-L4
COD removal (%)	87	90	90	89	93	88	92	93
CE (%)	10.2	10.7	8.6	2.5	5.8	5.7	5.3	3.9

to diffuse through the cathode, which accelerated substrate consumption by heterotrophic bacterial growth and other non-electricity generating processes, such as methanogenesis, denitrification, and aerobic respiration [12,28]. As shown in the test of the small MFC, the CE increased with increasing current density, which was consistent with previously reported results [8,9,26].

While CE indicates the recovery of electrons, the overall energy recovery of the system represents the energy harvested as electricity from bacteria vs. that lost to other processes. Normalized energy recovery (NER) is a proper representation of the energy performance of MFCs. NER conveys energy information and does not directly depend on the MFC dimensions [29]. Therefore, for MFCs with power production as a major objective, NER is a suitable parameter for the purpose of comparison. As illustrated in Table 3,

the MFC with the L4 cathode achieved the highest NER of 0.185 kWh m^{-3}, which was much higher than the average value (<0.05 kWh m^{-3}) reported in a previous review [29]. The cathodes with PVDF DLs generally showed higher NERs than those with PVDF/carbon black DLs. The NER of the MFC with the L2 cathode was only slightly decreased when the reactor size was scaled up from 28 mL to 700 mL, indicating that scale-up the MFC reactor had little impact on the NER. The NER data exhibited some discrepancies with respect to the power densities obtained in the presented study. The NER data expressed based on COD removal have profiles similar to those of NER data based on anode liquid volume.

3.6. Water loss

The DLs were applied on the base layer so that water loss from the cathodes can be reduced. The cathodes with pure PVDF DLs showed great waterproof performance. Water evaporation loss was not detectable even for the cathode with only two DLs. However, for the cathodes with PVDF/carbon black DLs, the water losses were remarkable, ranging from a 17.4 mL loss per day with one DL to a 9.9 mL loss per day with four DLs. Therefore, the cathodes with carbon black-blended DLs are not suitable for practical application in MFCs.

3.7. Cost analysis

The current commercial price of PVDF granules is $12,500 per ton, and the concentration of the PVDF solution we used was 18%, which means a cost of $0.8 per m^2 of the DLs in the cathode. Although the price of PTFE ($8,400 per ton) is lower than that of PVDF, a higher concentration of PTFE (60%) is required to fabricate the PTFE cathode, causing the cost of PTFE to reach as high as $2.2 per m^2. As a result, the use of PVDF is more cost-effective than the use of PTFE. Furthermore, the carbon cloth used here was non-waterproof and cheaper than the 30% waterproof carbon cloth currently used for cathode fabrication [9]. Therefore, the use of PVDF on carbon cloth would reduce the costs of cathode fabrication. However, the noble metal (Pt) catalyst used in this study is not cost-effective in saleable application. Thus, an inexpensive catalyst, such as activated carbon, should be employed in future studies of the practical application of these cathodes [30]. According to the results of our study, PVDF seems to be a promising DL material for MFC cathodes that can not only improve MFC performance but also reduce capital costs. (The current prices of PVDF and PTFE were provided by Dongyue Group Ltd., China).

4. Conclusions

Using PVDF in cathode DLs on a carbon base is a cost-effective technology. The results of our study showed that PVDF is a promising alternative to PTFE for single-chamber MFCs. Impedance tests showed that cathode with four PVDF DLs showed better performance based on reduced impedance, ensuring the cathode produced the highest MPD (0.123 mW cm^{-2}) and exhibited the best CE (10.7%). The cost-effective PVDF and carbon cloth make this cathode suitable for wastewater treatment and bioenergy production.

Table 3
Normalized energy recovery of MFCs with the cathodes.

Cathode type	700 mL								28 mL
	L2	L4	L6	L8	C-L1	C-L2	C-L3	C-L4	L2
NERs (kWh m^{-3})	0.165	0.185	0.131	0.035	0.107	0.010	0.091	0.060	0.184
NERs (kWh kg^{-1} COD)	0.165	0.180	0.129	0.035	0.103	0.010	0.088	0.058	0.172

Nevertheless, to further reduce the cost of cathodes, new supporting materials such as stainless steel mess and stainless steel felt and a less expensive catalyst such as activated carbon will be the focus of future research.

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